# CO<sub>2</sub> and O<sub>2</sub> MMV framework to quantify potential leaks from geosequestration: Technologies for detection for risk abatement

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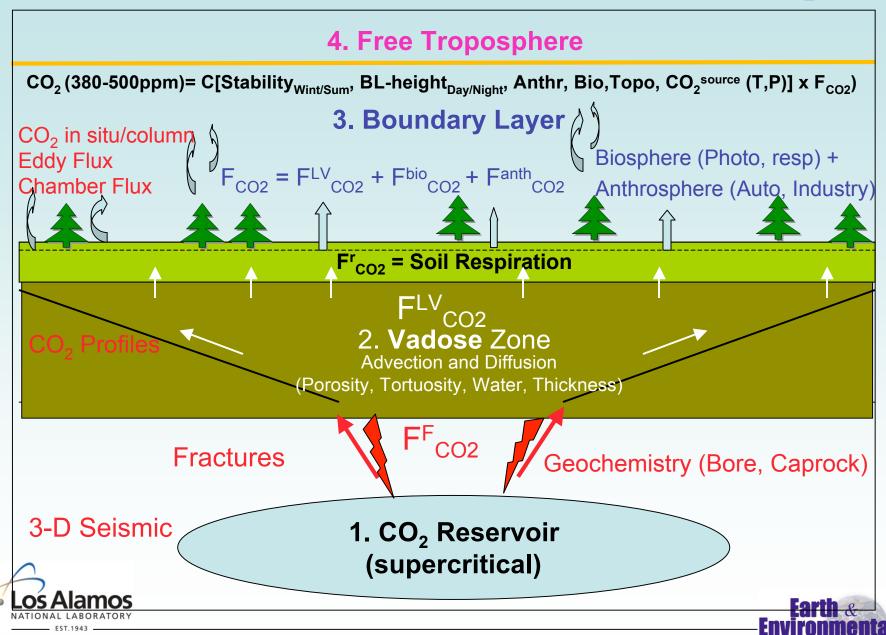
# Outline: MMV Framework for early detection and risk abatement

- Potential CO<sub>2</sub> Leak Scenario
  - Scale, Leak Rate, Footprint, Constraints
  - Fluxes and foot-print: Implications for leaks
- CO<sub>2</sub> Measurement Technologies (scales)
  - Chamber (m), Eddy Flux (10m-km), Remote (10kms-100kms)
- Mammoth Mountain: Natural Analogue
  - Technology applications and integration of results
- Separating Leak from natural background: Strategies
  - Time dependence (diurnal, seasonal)
  - Chemical fingerprinting of CO<sub>2</sub> leak (O<sub>2</sub>/CO<sub>2</sub>)
  - Tracers: <sup>14</sup>CO<sub>2</sub>, perfluorocarbons, <sup>13</sup>CO<sub>2</sub>
- Atmospheric modeling: Leaks to Concentrations
  - Background (vegetation, urban), orography, meteorology
- Mexico City: Urban Analogue





#### Leak Mechanisms and Paths: Reservoir to Atmosphere



#### Potential Storage and Leak Scenario for Detection Metric

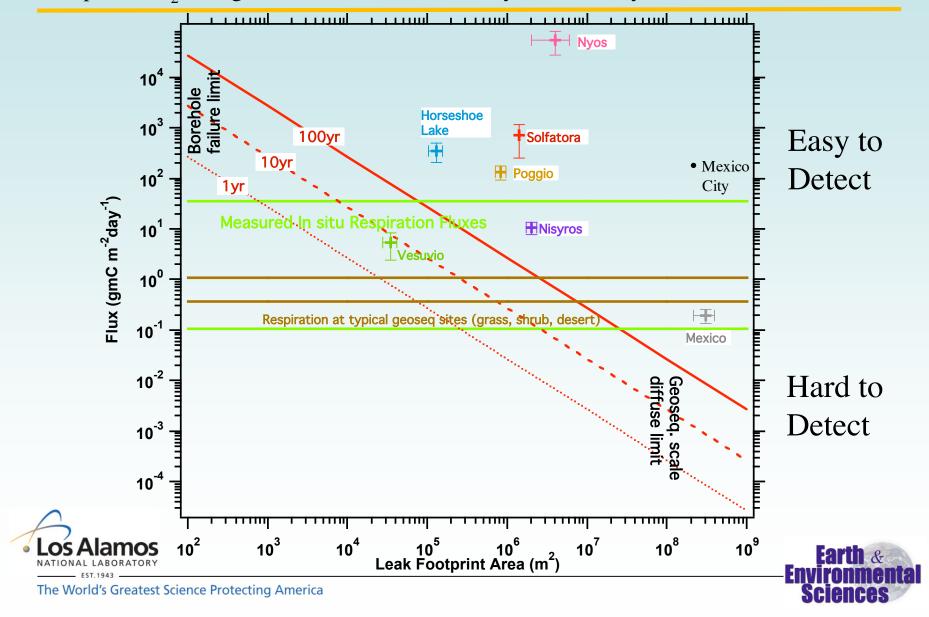
- 1 Megawatt zero emission coal fired power plant
- 3.6 Mtons CO<sub>2</sub>/year captured and sequestered
- ~ 4 times Sleipner and Weyburn sequestration rates
- Time horizons of 1, 10 and 100 years
- Reservoir size 3.6, 36 and 360 Megatons of CO<sub>2</sub>
- Leak rate 0.01%/year of reservoir size
- Spatial scale of sequestration site ~ 10 km
- Leak flux ~ (Leak rate)/(Leak path area)
- Leak path area variable: bore type~10<sup>2</sup> m<sup>2</sup> to diffuse~10<sup>8</sup> m<sup>2</sup>





#### Leak Flux vs footprint compared to natural/city analogues

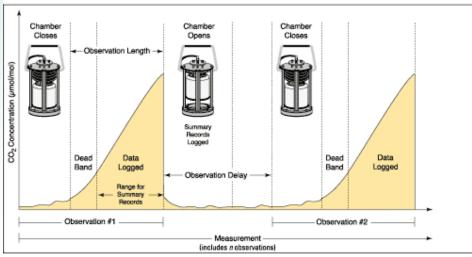
1 MW plant CO<sub>2</sub> storage reservoir after 1, 10, 100 yrs at 0.01%/year leak rate, 10km scale



#### Accumulation Chamber Measurements of CO<sub>2</sub> Flux



**LICOR-8100** 



Scale ~ 0.1 to 1m<sup>2</sup> Commercial Cost \$20K/unit Labor Intensive



#### Valles Caldera Grasslands: LANL Eddy Flux Site



Flux =  $\langle v(t)CO_2(t) \rangle$ 3-D sonic anemometer Open path NDIR  $CO_2$  at 10 Hz

<u>Goal</u>: Determine how grazing influences carbon sequestration.

Methodology: The covariance of simultaneous, collocated, high frequency measurements of vertical velocity and CO<sub>2</sub> concentrations can provide CO<sub>2</sub> surface fluxes under turbulent conditions.

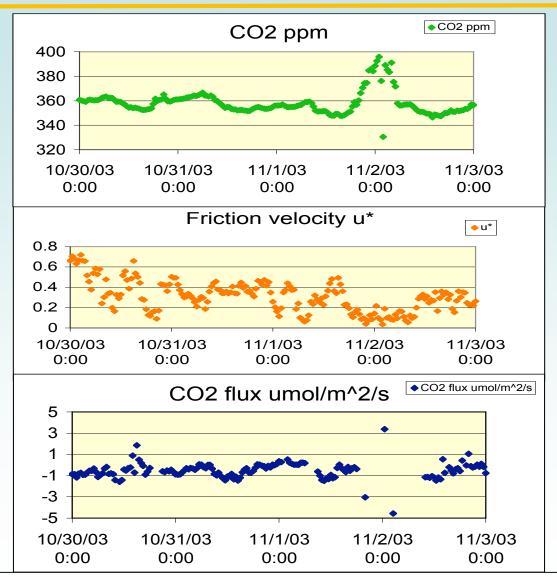
Fetch is  $\sim$  Horizontal velocity x tower height upwind (3m x 4m/s  $\sim$  12m), scales with tower height (400m  $\sim$  1.6km).

Cost \$50K/unit, automated but extensive data analysis is required.





#### Typical CO<sub>2</sub> Eddy Flux Data



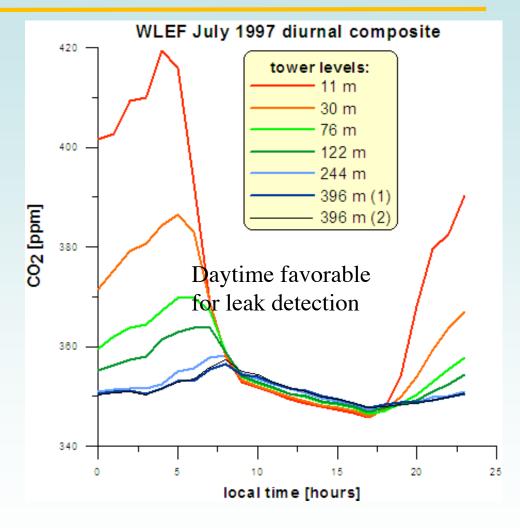




#### Diurnal Cycle of CO<sub>2</sub> at Wisconsin LEF (400m)



Fetch ~ 400m, 1.6 km of scale as geosequestration sites







#### Ground-based solar absorption (FTS) of column CO<sub>2</sub>/O<sub>2</sub>

CO<sub>2</sub> Column (10<sup>21</sup> molecules cm<sup>-2</sup>)

CO2 VMR (ppmv)

360

5.7

a)



Figure 4. A Bruker FTS is housed inside a 20 -foot shipping container. The facility is fully automated. Currently located at Caltech, it will be shipped to Park Falls, WI in early May.

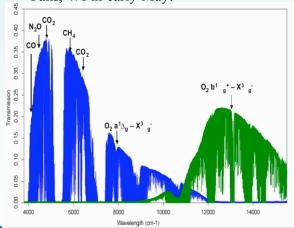
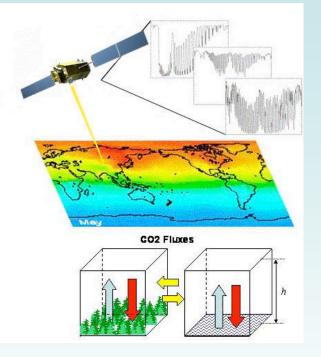


Figure 5. Near IR spectra of the sun obtained at Caltech. Absorption by numerous trace gases are obvious. Two room-temperature detectors are recorded simultaneously: blue - InGaAs: Green - Si.

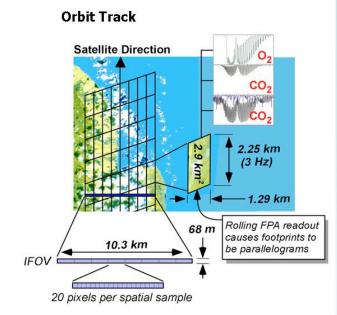
Figure 6. Measurements of the column O <sub>2</sub> (top), CO<sub>2</sub> (middle), and the ratio CO <sub>2</sub>/O<sub>2</sub> from Spectra obtained at Kitt Peak.

Can detect ~ppm change in column! Fetch ~ few km

#### **Observing Carbon Observatory Satellite: Launch in 2008**

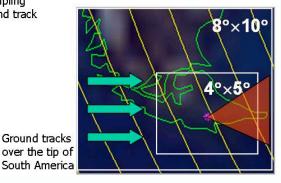


FT-NIR of sunlight reflected by earth



Spatial Sampling along ground track

Global Coverage, Sunsychronous orbit 1.18 pm observation at each location every day Fetch of raw spectral data about 3km x 3km Product 1x1 deg CO<sub>2</sub> column to 1ppm





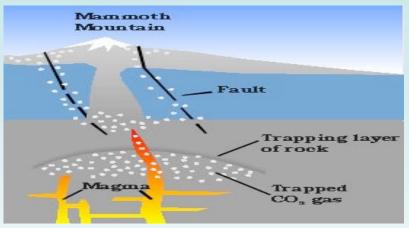
http://oco.jpl.nasa.gov/



#### UNCLASSIFIED

## Mammoth Mountain: Natural laboratory for understanding and monitoring CO<sub>2</sub> leakage from geo-sequestration

200 kyr old Dormant Volcano in Sierra Nevada active 700 yr ago

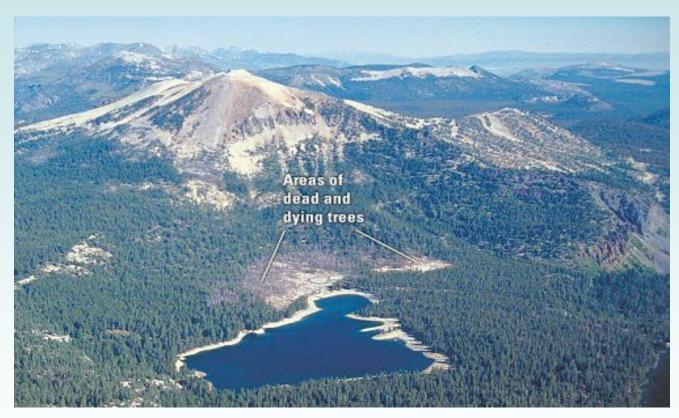


- 1990, series of earthquake swarms (6 months) initiate CO<sub>2</sub> degassing
  - Magmatic CO<sub>2</sub> reservoir at 2-4 km depth
  - High permeability soils; Faults/fractures enhance permeability
  - Tree kills (Horseshoe lake) observed over large areas
  - Toxic CO<sub>2</sub> levels (15-90%) common in soil and snow pack
  - CO<sub>2</sub> in air above depressions can accumulate to lethal levels (skier deaths, '98 & '06)
  - Extensively studied by chamber, eddy-flux, aircraft campaigns





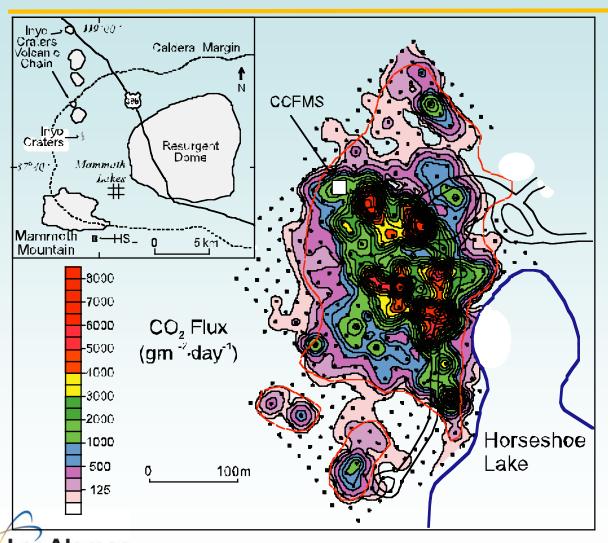
#### Tree kills at Mammoth Mountain, CA



Ecological impacts of  $CO_2$  leaks are real and should be addressed.  $CO_2$  induced asphyxia has killed people (3, few weeks ago)



## **Accumulation Chamber Observations of CO<sub>2</sub> fluxes**



Grid of 425 chambers.

Soil biological flux is <15 g m<sup>-2</sup> d<sup>-1</sup>, used 25 g m<sup>-2</sup> d<sup>-1</sup> cutoff for magmatic CO<sub>2</sub> efflux

Net Flux: 133 tons/day

Footprint: 200m x 500m

~100,000 m<sup>2</sup> area

<Flux>: 1330 g m<sup>-2</sup> d<sup>-1</sup>

Highest: 8000 g m<sup>-2</sup> d<sup>-1</sup>

Rogie et al. EPS 2001

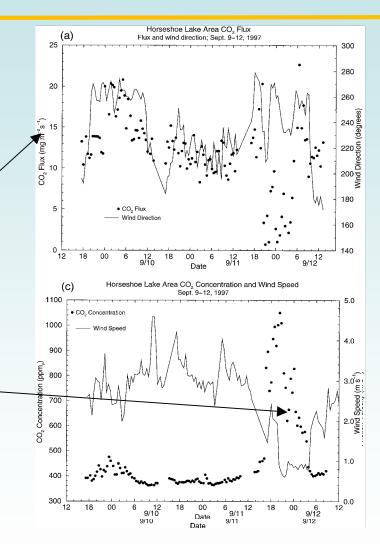


#### **Eddy Flux Observations at HSL (1996-1998)**

2 m height

Fluxes 700-1400 g m<sup>-2</sup> d<sup>-1</sup> / comparable to chamber studies

High wind dissipates CO<sub>2</sub> from boundary layer by mixing —





Anderson & Farrar Chem. Geol. '01



#### Chemically Fingerprinting CO<sub>2</sub> Source Plume Using O<sub>2</sub>

Respiration & Combustion produce CO<sub>2</sub> and consume  $O_2$  stoichiometrically (~1:1) e.g.  $C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$ 

Stored CO<sub>2</sub> should have negligible CO<sub>2</sub> Leaks increase CO<sub>2</sub> without influencing O<sub>2</sub>

> O<sub>2</sub>/CO<sub>2</sub> measured in air at Trinidad traced N. California fires 10/8 to 10/21 1990 plumes, 70 km away. Can discriminate smoky and flaming fires from slope.

> > Lueker, Keeling, Dubey UCSD-LANL, GRL-2001

#### Wilfire data

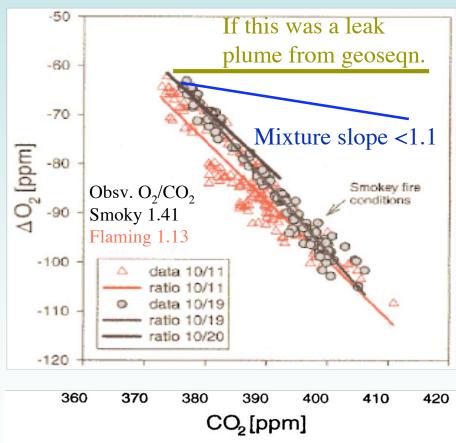
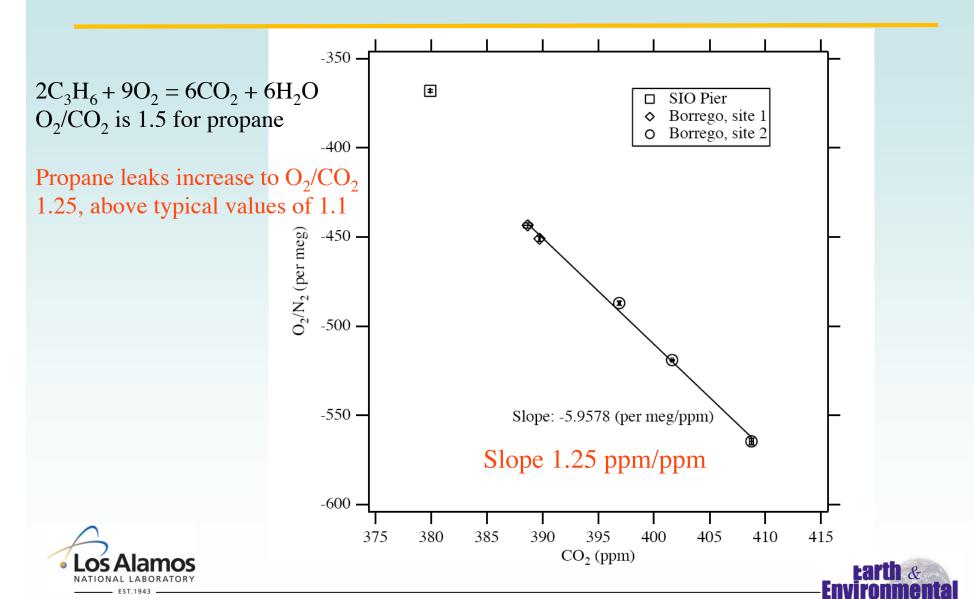


Figure 2. Changes in atmospheric O<sub>2</sub> vs. changes in CO<sub>2</sub> observed on 10/11 and 10/19. O2 changes expressed in units equivalent to  $CO_2$ , i.e. ppm = (per meg / 4.8).

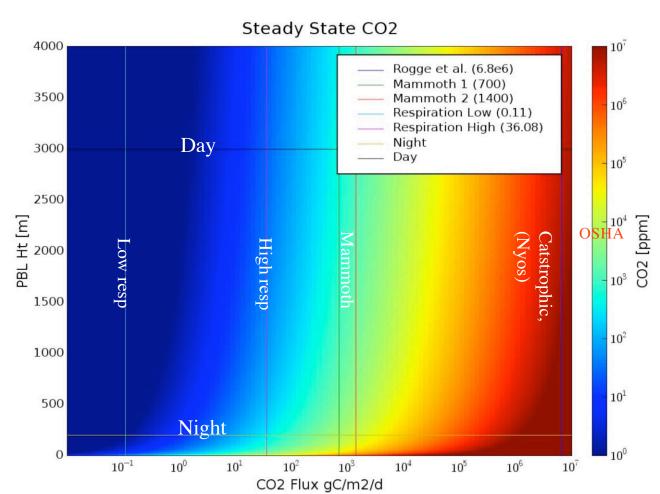


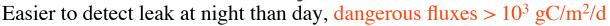
#### **Proof of principle: Fingerprint Propane Leaks Borrego CA**



#### Sensitivity of atmospheric CO<sub>2</sub> to leak flux

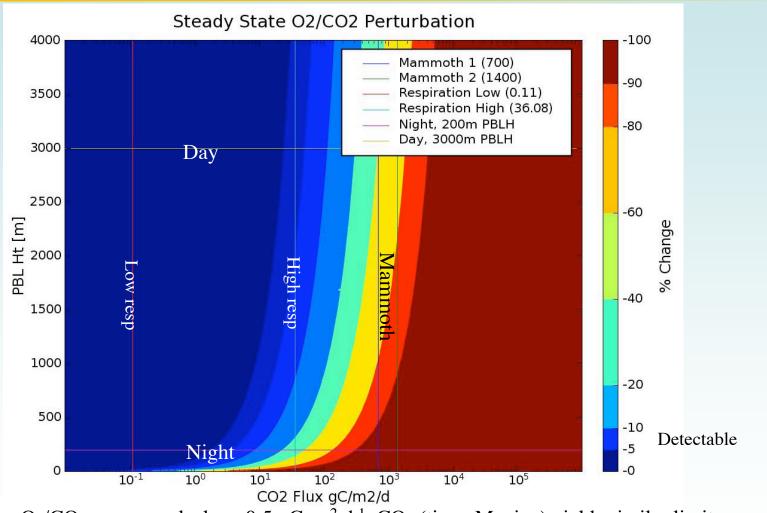
#### Single planetary boundary layer box at steady state







#### Sensitivity of O<sub>2</sub>/CO<sub>2</sub> to Leak: Single Box Model



 $O_2/CO_2$  can sense leaks > 0.5 gC m<sup>-2</sup> d<sup>-1</sup>,  $CO_2$  (time, Mexico) yields similar limit



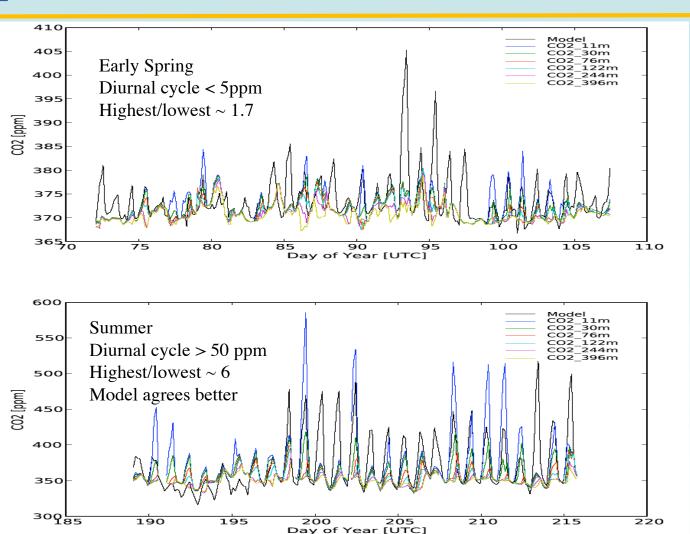
#### **Atmospheric CO<sub>2</sub> Modeling: Fluxes to Concentrations**

- Mixed layer Model: Boundary layer (BL) and Free troposphere (FT)
- BL shallow at night and deepens during day by solar heating
- BL depth from NASA, GMAO, GEOS-1 data-model assimilation
- Constrained by surface winds and water fields
- BL shallow at night and grows during daytime
- Applicable to diffuse leaks in flat terrain with large footprint
- Our simulations are compared with WLEF tower data
- Assessment of leak detection at geosequestration sites





#### CO<sub>2</sub> Simulations vs Observations at WLEF tower



Seasonal signal can be exploited for leak detection



Active

Higher

Biosphere

fluxes and

variability

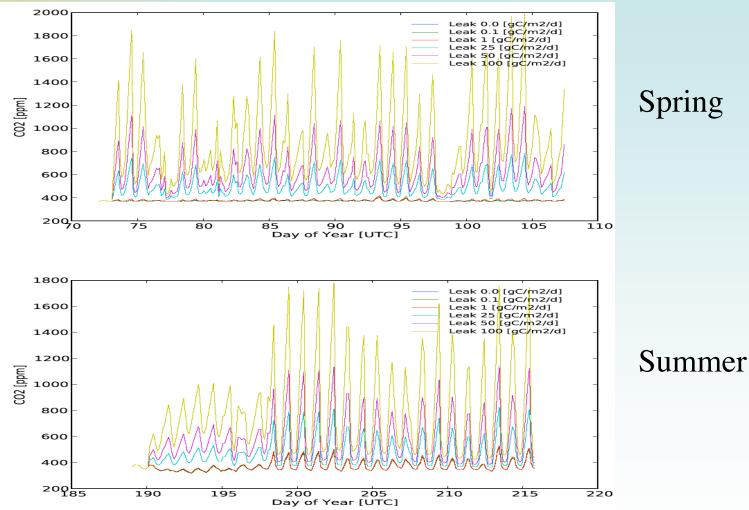
Dormant

Biosphere

Lower fluxes

and variability

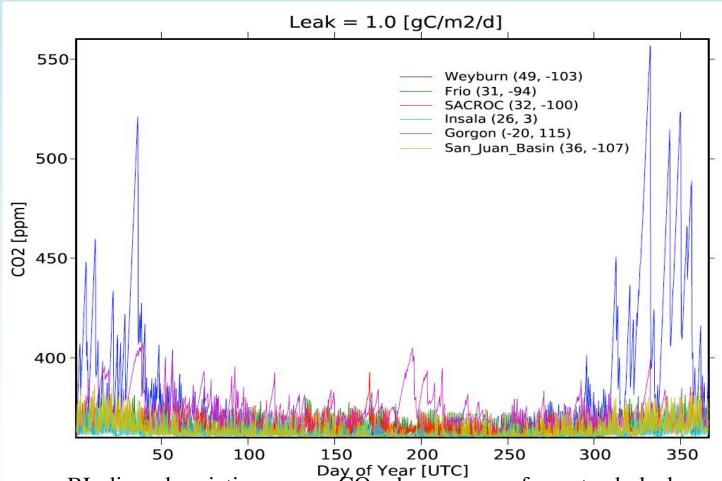
#### Simulated leak detection sensitivities at WLEF



Leaks < 1gCm<sup>-2</sup>d<sup>-1</sup> unresolvable, > 25gCm<sup>-2</sup>d<sup>-1</sup> clear, spring easier than summer

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#### Leak detection sensitivity for geoseqn. sites

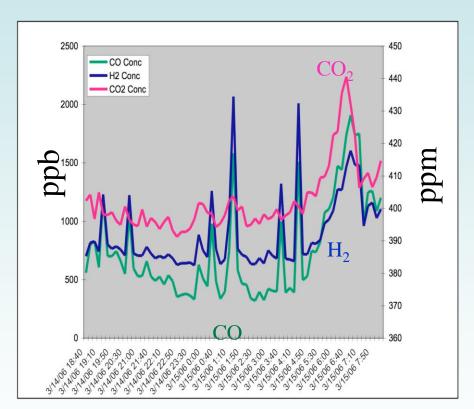


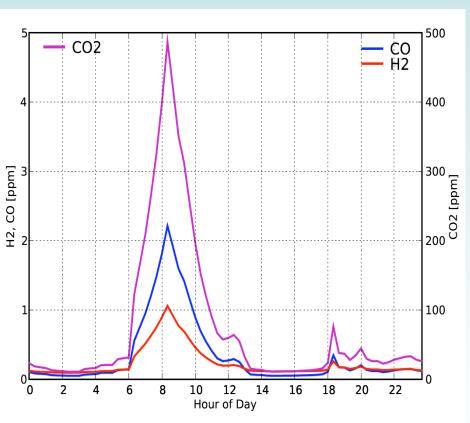
BL diurnal variations cause  $CO_2$  changes even for a steady leak Largest  $CO_2$  increases in winter, especially at Weyburn site Increases of > 10 ppm above 350 ppm baes are clear at all sites

#### Urban Analogue: Mexico Mega City CO<sub>2</sub> sources

Observations: MILAGRO 3/06

WRF-CHM Model (3 km res)





 $\rm CO_2$  Emissions~380,000 tons/yr, Area ~ (30km x 10km), Flux~0.2 gC m<sup>-2</sup> d<sup>-1</sup> Time dependence of auto emission allows clear resolution of this leak



## **Conclusions**

- Realistic leak scenarios constructed
  - Leak fluxes estimated as a function of leak path footprint areas
  - Compared with natural and urban analogues to quantify risks
- Technologies for leak detection surveyed (LANL expertise!)
  - Commercially available, affordable, and mature
  - Leaks from meter to kilometer scale can be monitored
  - Flux, surface & column concentration measurements can detect leaks
- Mammoth mountain studies: Mature detection technologies
  - Chamber surveys, eddy-flux, aircraft measurements "consistent"
  - Fluxes are high ~1-10 kg m<sup>-2</sup> day-1, Footprint 100,000-500,000 m<sup>2</sup>
- Early detection of leaks within natural background possible
  - Exploit temporal differences (diurnal, seasonal, ned baseline)
  - Chemical fingerprinting of leaks (e.g. O<sub>2</sub>/CO<sub>2</sub>, tracers)
- Atmospheric model to determine CO<sub>2</sub> increase from fluxes
  - Early detection and risk abatement is easier at current geoseqn. sites

